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[54] **LOW PH GERMICIDAL IODINE COMPOSITIONS HAVING ENHANCED STABILITY**

[75] Inventors: **Michael D. McKinzie; Murray W. Winicov**, both of Kansas City, Mo.

[73] Assignee: **West Agro, Inc.**, Kansas City, Mo.

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[58] Field of Search **424/667, 668, 424/669, 80**

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Primary Examiner—Phyllis G. Spivak
Attorney, Agent, or Firm—Hovey, Williams, Timmons & Collins

[57] **ABSTRACT**

Stable aqueous iodine/iodide/iodate germicidal compositions are provided which have relatively high quantities of free iodine therein and also substantially maintain the starting amounts of available and free iodine throughout a storage period of at least about three months. The compositions of the invention contain from about 0.01-1.4% by weight available iodine, from about 10-125 ppm free iodine, from about 0.005-0.5% by weight iodate ion, from about 0.1-15% by weight of iodine complexing agent, from about 0.004-0.5% by weight iodide ion, and have a pH of from about 2.0-4.5.

35 Claims, No Drawings

LOW PH GERMICIDAL IODINE COMPOSITIONS HAVING ENHANCED STABILITY

Background of the Invention

1. Field of the Invention

The present invention is broadly concerned with aqueous germicidal iodine/iodide/iodate compositions of very low pH (from about 2–5.5) having enhanced available iodine and free iodine stabilities over extended storage periods of at least about three months. More particularly, the invention pertains to such compositions which contain from about 0.01–1.4% by weight available iodine, from about 10–125 ppm free iodine, from about 0.004–0.50% by weight iodide ion, and from about 0.005–0.5% by weight iodate ion, in combination with an iodine complexing agent. Optional ingredients may include emollients, buffering agents and thickeners.

2. Description of the Prior Art

U.S. Pat. No. 4,271,149 describes aqueous detergent-iodine compositions of the iodine/iodide/iodate variety having pH values of 5–7 with elemental iodine amounts up to about 1% by weight. Typically, representative compositions described within the '149 patent will have free (i.e., uncomplexed) iodine levels of less than 10 ppm. In compositions of this type, two primary competing reactions take place during storage to maintain stability. First, there is some conversion of elemental iodine in the presence of organic matter to iodide ion; second, there is a competing reaction between iodate ion, iodide ion and H^+ to form I_2 . Ideally, these two reactions are balanced so that the I_2 content of the compositions remains essentially constant.

In recent years, users of germicidal iodine compositions have requested greater and greater amounts of free iodine, e.g., about 20 ppm and above. In order to meet this demand, it is necessary to lower the pH levels of the compositions to achieve these higher free iodine concentrations. However, it was known that at low pH values below 5, the reaction between iodide and iodate to form elemental iodine becomes predominant and can generate excessive amounts of iodine. Hence, products of the type described in the '149 patent, at low pH, would lack requisite long-term stability. Workers in the art have thus faced a heretofore insoluble dilemma: by lowering the pH to achieve and maintain desired higher free iodine levels, the stability of the compositions is very significantly affected, particularly over long storage times.

There is accordingly a real and unsatisfied need in the art for improved aqueous germicidal use compositions of the iodine/iodide/iodate variety which are of very low pH in order to generate/maintain high free iodine levels therein and which are stable over long periods of storage.

SUMMARY OF THE INVENTION

The present invention overcomes the problems outlined above and provides low pH, stable aqueous detergent-iodine germicidal use compositions having a pH of from about 2–5.5 and a free iodine content on the order of 10–125 ppm while retaining acceptable ranges of available iodine and free iodine contents over a room temperature storage period of at least about three months, and more preferably at least about one year. Preferably, substantial maintenance of the amounts of available and free iodine refers to the ability of the compositions to maintain the nominal, as-manufactured amounts of free and available iodine within about $\pm 20\%$.

Broadly speaking, the compositions of the invention both as originally formulated and after an equilibration period of

about one week, include from about 0.01–1.4% by weight available iodine. In the case of hard surface sanitizers, the as-manufactured available iodine content is preferably from about 0.01–0.20% by weight, whereas for topical skin applications, the available iodine has a range of from about 0.10–1.4% by weight. The free iodine content should be from about 10–125 ppm and more preferably from about 25–125 ppm. The iodate ion content of the compositions should be at a level of from about 0.005–0.5% by weight and more preferably from about 0.01–0.4% by weight. The iodide ion content should be from about 0.004–0.50% by weight, and more preferably from about 0.01–0.45% by weight. The pH levels of the compositions should be from about 2–5.5 and more preferably from about 2–4.5.

A prime advantage of the compositions of the invention is the maintenance of extremely high levels of free iodine over extended storage periods. As indicated above, the free iodine content should broadly be from about 10–125 ppm. In more preferred forms, the compositions of the invention maintain a free iodine level of at least about 25 ppm over a storage period at ambient temperature of at least about 3 months, and most preferably at least about 40 ppm. Thus, in the case of hard surface sanitizers, it is desired that they exhibit a free iodine content of at least about 40 ppm over at least a 3 month ambient temperature storage period. For some preparations adapted for topical application to skin, it may be desirable to maintain the free iodine content at a level of from about 20–50 ppm over an ambient temperature storage period of at least 3 months.

The compositions hereof also include a complexing agent which is used in sufficient quantity to insure that the available iodine content of the compositions remains in solution. Generally, the complexing agent should be used at a level of from about 0.1–15% by weight, and more preferably from about 0.2–10% by weight. A variety of complexing agents can be employed, such as those selected from the group consisting of the alkylphenol ethoxylates, alcohol ethoxylates, alcohol alkoxyates, polyalkylene glycol ethers, polyoxyethylene sorbitan monolaurate and monopalmitate, polyvinylpyrrolidone, polyethoxylated polyoxypropylenes, and mixtures thereof.

Normally, compositions in accordance with the invention would include a buffering agent such as an acid selected from the group consisting of citric, acetic, propionic, lactic, phosphoric, salts of the foregoing, and mixtures thereof. Such a buffering agent would normally be used at a level of from about 0.02–1% by weight in order to maintain the desired pH level during extended storage. For ease of use, a thickening agent may also be incorporated into the compositions of the invention. Suitable thickening agents may be selected from the group consisting of the alginates, xanthan gums, cellulose-bearing agents and mixtures thereof, and would ordinarily be used at a level of from about 0.05–1.5% by weight. Emollients are also commonly used in compositions of the invention, such as those selected from the group consisting of glycerine, lanolin and its derivatives, sorbitol, fatty acid esters of polyhydroxylated compounds, propylene glycol, and mixtures thereof. The emollient content would typically be in the range of from about 1–15% by weight.

There are several ways in which the compositions of the invention can be prepared. Generally speaking, in view of the low levels of iodide employed, it may not be convenient to start with a liquid concentrate having the desired iodide:iodine ratio. However, it is possible to start with iodide alone, and to form the desired portion of iodine in situ through oxidation. Alternately, one may employ a concen-

TABLE 1-continued

	1% Available Iodine (Nominal)									
	1	2	3	4	5	6	7	8	9	10
Iodine Complex A ¹	3.3	3.3	2.7	2.7	2.7	2.7	2.83	2.83	2.83	2.83
Iodide	—	—	.15-.25	.15-.25	.15-.25	.15-.25	.15-.25	.15-.25	.15-.25	.15-.25
Citric Acid	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Glycerin	10.0	6.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Sodium Iodate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%
Initial pH (Mfg.)	4.0	4.0	2.75	3.0	3.5	4.0	2.75	3.0	3.5	4.0
Initial pH (4 days)	4.4	4.4	3.03	3.25	3.67	3.42	3.67	4.01	4.36	
2 Mos. pH	4.6	4.6	3.47	3.67	4.10	4.42	3.66	3.89	4.02	4.56
4 Mos. pH	4.8	4.8	3.56	3.71	4.12	4.43	3.71	3.90	4.20	4.50
Initial Available I ₂	1.00	1.00	.94	.93	.91	.88	.94	.95	.93	.91
2 Mos. Available I ₂	1.02	1.01	.97	.97	.95	.93	.96	.99	1.00	.97
4 Mos. Available I ₂	1.05	1.00	1.08	1.05	.99	.97	1.04	1.05	1.03	1.02
Initial Free I ₂ (ppm)	10	8	51	56	37	22	56	41	27	12
2 Mos. Free I ₂ (ppm)	17	12	77	60	39	24	67	48	31	10
4 Mos. Free I ₂ (ppm)	18	16	67	52	35	22	53	42	27	20

¹The iodine complex A had an available iodine content of from about 27.5–29.5% by weight and a total iodine content of 37.0–41.0% by weight.

TABLE 2

	0.75% Available Iodine (Nominal)	
	11	12
Povidone K-30	—	—
Nonoxynol 10	—	—
Poloxamer 335	3	3
Available Iodine	0.75	0.75
Iodide	0.09	0.1
Citric Acid	0.1	0.1
Glycerin	0.5	0.5
Sodium Iodate	0.1	0.1
Water	q.s. 100%	q.s. 100%
Initial pH	4.1	4.5
3 Mos. pH	4.4	4.6
Initial Available I ₂	.70	.70
3 Mos. Available I ₂	.71	.70
Initial Free I ₂ (ppm)	30	29
3 Mos. Free I ₂ (ppm)	42	29

TABLE 3

	0.50% Available Iodine			
	13	14	15	16
Poloxamer 403	1.25	1.25	—	—
Povidone K-30	—	—	2.5	2.5
Iodine Complex A	1.50	1.50	1.50	1.50
Citric Acid	0.1	0.1	0.1	0.1
Glycerin	2.0	2.0	2.0	2.0
Sodium Iodate	0.2	0.2	0.2	0.2
Water	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%
Initial pH	3.5	4.0	3.5	4.0
3 Mos. pH	3.9	4.2	4.2	4.4
Initial Available I ₂	.51	.51	.50	.49
3 Mos. Available I ₂	.52	.51	.50	.49
Initial Free I ₂ (ppm)	31	22	27	19
3 Mos. Free I ₂ (ppm)	47	37	31	24

TABLE 4

	0.25% Available Iodine			
	17	18	19	20
Poloxamer 403	1.0	1.0	1.0	1.0
Iodine Complex B ¹	0.38	0.38	0.35	0.35
Citric Acid	0.1	0.1	0.1	0.1
Viscosity Agent ²	0.05	0.05	0.05	0.05
Glycerin	2.0	2.0	2.0	2.0
Sodium Iodate	0.1	0.1	0.1	0.1
Water	q.s. 100%	q.s. 100%	q.s. 100%	q.s. 100%
Initial pH	3.6	3.3	4.0	3.6
3 Mos. pH	3.6	3.4	4.1	3.5
Initial Available I ₂	.25	.22	.24	.22
3 Mos. Available I ₂	.26	.24	.25	.24
Initial Free I ₂ (ppm)	13	19	10	17
3 Mos. Free I ₂ (ppm)	21	16	24	23

¹Iodine Complex B had an available iodine content of from about 56.0–58.0% by weight and a total iodine content of 75.0–79.0% by weight

²Xanthan gum

TABLE 5

	0.10% Available Iodine						
	21	22	23	24	25	26	27
Poloxamer 335	—	—	—	—	0.25	0.25	—
Polysorbate 80	—	—	—	—	0.2	0.2	—
Poloxamer 403	—	—	—	—	—	—	0.5
Povidone K-30	0.25	0.50	1.0	1.0	—	—	—
Iodine Complex A	0.30	0.30	0.30	0.30	0.30	0.30	0.32
Citric Acid	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Glycerin	0.15	0.15	0.15	0.15	2.05	2.0	2.0
Sodium Iodate	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
	100%	100%	100%	100%	100%	100%	100%
Initial pH	3.0	3.0	3.0	2.7	3.8	3.7	3.0
3 Mos. pH	3.6	3.6	3.6	2.8	4.6	4.4	3.3
Initial Available I ₂	.09	.09	.09	.09	.09	.08	.10
3 Mos. Available I ₂	.10	.10	.10	.12	.11	.10	.11
Initial Free I ₂ (ppm)	44	40	37	68	14	14	—
3 Mos. Free I ₂ (ppm)	52	46	42	78	17	16	53

TABLE 6

	0.05% Available Iodine				
	28	29	30	31	32
Nonoxynol 12	0.50	0.50	0.50	—	—
Povidone K-30	—	—	—	0.10	0.20
Iodine Complex A	0.15	0.15	0.15	0.15	0.15
Citric Acid	0.05	0.05	0.05	0.05	0.05
Sodium Iodate	0.1	0.1	0.1	0.05	0.05
Water	q.s.	q.s.	q.s.	q.s.	q.s.
	100%	100%	100%	100%	100%
Initial pH	3.0	2.7	2.4	2.2	2.2
3 Mos. pH	3.1	2.9	2.7	2.3	2.3
Initial Available I ₂	.05	.05	.05	.04	.04
3 Mos. Available I ₂	.04	.05	.03	.06	.05
Initial Free I ₂ (ppm)	55	55	66	87	77
3 Mos. Free I ₂ (ppm)	49	45	45	116	115

TABLE 7

	0.025% Available Iodine	
	33	34
Povidone K-30	0.1	0.1
Iodine Complex A	0.075	0.075
Citric Acid	.05	.05
Sodium Iodate	.05	.10
Water	q.s. 100%	q.s. 100%
Initial pH	2.0	2.0
3 Mos. pH	2.1	2.1
Initial Available I ₂	.025	.024
3 Mos. Available I ₂	.019	.023
Initial Free I ₂ (ppm)	114	104
3 Mos. Free I ₂ (ppm)	130	118

We claim:

1. A stable aqueous germicidal composition comprising:
 - from about 0.01–1.4% by weight available iodine;
 - from about 10–125 ppm free iodine;
 - from about 0.005–0.5% by weight iodate ion;

25 a quantity of complexing agent sufficient for maintaining said available iodine in solution; from about 0.004–0.50% by weight iodide ion; and said composition having a pH of from about 2.0–4.5 and substantially maintaining the amounts of said available iodine and free iodine over a period of at least three months at room temperature storage.

30 2. The composition of claim 1, said composition having an available iodine level of from about 0.01–0.2% by weight.

35 3. The composition of claim 1, said composition having an available iodine level of from about 0.10–1.4% by weight.

4. The composition of claim 1, wherein said free iodine level is from about 25–125 ppm.

40 5. The composition of claim 1, wherein said iodate ion level is from about 0.01–0.4% by weight.

6. The composition of claim 1, wherein said complexing agent is present at a level of from about 0.1–15% by weight.

45 7. The composition of claim 1, said composition substantially maintaining said amounts of available iodine and free iodine for a period of at least about one year.

8. The composition of claim 1, including a buffering agent selected from the group consisting of citric acid, acetic acid, propionic acid, lactic acid, phosphoric acid, salts of the foregoing, and mixtures thereof.

50 9. The composition of claim 8, said buffering agent being present at a level of from about 0.02–1% by weight.

10. The composition of claim 1, said complexing agent being selected from the group consisting of the alkylphenol ethoxylates, alcohol ethoxylates, alcohol alkoxyates, polyalkylene glycol ethers, polyoxyethylene sorbitan monolaurate and monopalmitate, polyvinylpyrrolidone, polyethoxylated polyoxypropylenes, and mixtures thereof.

11. The composition of claim 1, including a thickening agent.

60 12. The composition of claim 11, said thickening agent being selected from the group consisting of alginates, xanthan gums, cellulose-bearing agents, and mixtures thereof.

13. The composition of claim 11, said thickening agent being present at a level of from about 0.05–1.5% by weight.

65 14. The composition of claim 1, including an emollient.

15. The composition of claim 14, said emollient being selected from the group consisting of glycerin, lanolin,

sorbitol, fatty acid esters of polyhydroxylated compounds, propylene glycol, and mixtures thereof.

16. The composition of claim 14, said emollient being present at a level from about 1–15% by weight.

17. An aqueous germicidal composition which comprises
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respective amounts of available iodine, free iodine, iodate ion, iodide ion, and a complexing agent, said composition having at least about 25 ppm free iodine over a period of at least about 3 months at ambient temperature storage.

18. The use composition of claim 17, said composition
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having at least about 40 ppm free iodine over a period of at least 3 months at ambient temperature storage.

19. A stable aqueous germicidal composition comprising:

from about 0.01–1.4% by weight available iodine;

at least about 25 ppm free iodine;

from about 0.005–0.5% by weight iodate ion;

a quantity of complexing agent sufficient for maintaining
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said available iodine in solution;

from about 0.004–0.50% by weight iodide ion; and

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said composition having a pH of from about 2–5.5 and substantially maintaining the amounts of said available iodine and free iodine over a period of at least three months at room temperature storage.

20. The composition of claim 19, said composition having
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an available iodine level of from about 0.01–0.2% by weight.

21. The composition of claim 19, said composition having
an available iodine level of from about 0.10–1.4% by
weight.

22. The composition of claim 19, wherein said free iodine
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level is from about 25–125 ppm.

23. The composition of claim 19, wherein said iodate ion
level is from about 0.01–0.4% by weight.

24. The composition of claim 19, wherein said complexing agent is present at a level of from about 0.1–15% by weight.

25. The composition of claim 19, wherein said pH is from
about 2.0–4.5.

26. The composition of claim 19, said composition substantially maintaining said amounts of available iodine and free iodine for a period of at least about one year.

27. The composition of claim 19, including a buffering agent selected from the group consisting of citric acid, acetic acid, propionic acid, lactic acid, phosphoric acid, salts of the foregoing, and mixtures thereof.

28. The composition of claim 27, said buffering agent being present at a level of from about 0.02–1% by weight.

29. The composition of claim 19, said complexing agent
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being selected from the group consisting of the alkylphenol ethoxylates, alcohol ethoxylates, alcohol alkoxyates, polyalkylene glycol ethers, polyoxyethylene sorbitan monolaurate and monopalmitate, polyvinylpyrrolidone, polyethoxylated polyoxypropylenes, and mixtures thereof.

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30. The composition of claim 19, including a thickening agent.

31. The composition of claim 30, said thickening agent being selected from the group consisting of alginates, xanthan gums, cellulose-bearing agents, and mixtures thereof.

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32. The composition of claim 30, said thickening agent being present at a level of from about 0.05–1.5% by weight.

33. The composition of claim 19, including an emollient.

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34. The composition of claim 33, said emollient being selected from the group consisting of glycerin, lanolin, sorbitol, fatty acid esters of polyhydroxylated compounds, propylene glycol, and mixtures thereof.

35. The composition of claim 34, said emollient being present at a level from about 1–15% by weight.

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